Cationic Silver Bromide Complexes in Alkali Nitrate Melts.

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Potentiometric measurements of the free ligand concentration $[Ag^+]$ and solubility measurements have been used to investigate the formation of cationic complexes between silver(I) and bromide ions in fused equimolar $(K,Na)NO_3$ at 280 °C. No polynuclear (polybromic) species can be detected potentiometrically. The distribution of AgBr and $AgNO_3$ between solid solutions $Ag(Br,NO_3)$ and the nitrate melt indicates a stepwise formation of complexes $Ag_{\underline{m}}Br^{(\underline{m}-1)+}$ with $\underline{m}$ = 2, 3 and 4. The corresponding stability constants have been evaluated from the solubility data.

The formation and thermodynamic stability of neutral and anionic silver bromide complexes in alkali nitrate melts have been studied previously at this laboratory.[1-3] From studies in aqueous solution - mostly by solubility measurements[4-8] - the ability of silver and bromide ions to form cationic complexes $Ag_{\underline{m}}Br^{(\underline{m}-1)+}$ has become evident. Analogous chloride and iodide complexes with ion charges +1, +2 and +3 have also been suggested in aqueous solution[5-7,9-12] and strong evidence for similar ions in polar organic solvents has emerged as well.[13-15]

Solid compounds of the general formulae $Ag_{\underline{m}}XA_{(\underline{m}-1)}$ (X = Cl, Br or I and A = NO_3, ClO_4 or F) have been prepared from aqueous solutions[7,16-21] and from anhydrous melts.[22-26]

In some binary melts AgX-$AgNO_3$ the existence of cationic silver halide species has been suggested.[26-28] In ternary systems so-called "dinuclear" species Ag_2X^+ have been proposed as an interpretation of emf data obtained in fused alkali or alkaline earth metal nitrates. Thus, evidence for Ag_2Cl^+ and Ag_2Br^+ has been found in a number of nitrate media,[29-35] and Guion[36] explained the results from similar emf measurements in molten eutectic $(K,Li)_2SO_4$ by assuming the presence of Ag_2Br^+. The emf method that was solely used in these investigations[29-36] is, however, not very convenient for studying relatively weak cationic complexes, since - in general - the measured concentration of free ligand, $[Ag^+]$, does not differ very much from the total ligand concentration $\underline{C}_{Ag}$. Furthermore, the fraction of halide ion present as Ag_2X^+ has often been small, making an accurate evaluation of the corresponding stability constant impossible.[37,38]

A more convenient method is to study the solubility of a silver

halide in melts containing various amounts of e.g. $AgNO_3$. Seward and Field[39] used this method to indicate the presence of Ag_2Cl^+ in fused $NaNO_3$ and Sinistri and Pezzati[40] have made a more extensive study of silver chloride and bromide complexation in equimolar $(K,Na)NO_3$ employing the solubility method. They found evidence for complex ions with net charges +1 and +2 and determined the stability constants for the proposed species Ag_2X^+ and Ag_3X^{2+}.

This study of systems $AgBr-AgNO_3-(K,Na)NO_3$ has been undertaken in order to complete the picture of the silver bromide complexation in nitrate melts and to compare the results with those from aqueous media with respect to relative stability of different species and to the maximum number of silver(I) ligands attached to a bromide central ion.

The study is restricted to the range 0.2 mol $kg^{-1} < \underline{C}_{Ag} < 2$ mol kg^{-1}, which is of primary interest as far as only positively charged complexes are concerned. In contrast to what has been found for dissolution of alkali halides in solid AgI[41] and AgBr[3], it appeared that the solubility of $AgNO_3$ in solid AgBr was rather small. Nevertheless it was analytically significant and the composition of both phases have been determined. The activity of AgBr in the solid is computed as described recently.[3]

In the region 0.8 mol $kg^{-1} \leq \underline{C}_{Ag} \leq 2.4$ mol kg^{-1} the free ligand concentration $[Ag^+]$ has been directly determined from emf measurements with cells of the two general types

I: Ag $Ag(Br,NO_3)(s)$	$\underline{C}'_{Ag}$ $AgNO_3$ $\underline{C}_{Br}$ AgBr (saturated) $(K,Na)NO_3$	asbestos fibre	$\underline{C}^{o}_{Ag}$ $AgNO_3$ $(K,Na)NO_3$	Ag

II: Ag | $\underline{C}'_{Ag}$ $AgNO_3$, $\underline{C}_{Br}$ AgBr (unsaturated), $(K,Na)NO_3$ | asbestos fibre | $\underline{C}^{o}_{Ag}$ $AgNO_3$, $(K,Na)NO_3$ | Ag

From the emf data the average ligand number $\bar{n}$ can be calculated with an accuracy good enough to provide a semi-quantitative picture of the complex formation at high ligand concentrations, which assists the interpretation of the solubility data.

EXPERIMENTAL

Chemicals. All chemicals were p.a. grade and prepared and stored as described previously.[3,41]

Apparatus. The equipment used for the solubility and emf measurements has been described in Ref. 3 and Refs. 42 and 43, respectively.

Procedure. Solubility measurements: Systems containing 75.00 g equimolar $(K,Na)NO_3$, 12 g AgBr and various amounts of $AgNO_3$ were agitated for at least 50 h until equilibrium was attained (as concluded from constant solubility). Samples were withdrawn from the nitrate phase and analysed for silver and bromide.

Emf measurements: In the study of unsaturated melts the electrode function was checked by measuring emfs after adding successive portions of $AgNO_3$ to the left hand compartment of cell II, keeping $\underline{C}_{Br} = 0$. Silver bromide was then dissolved in the melt, and the titration with $AgNO_3$ was continued to $\underline{C}_{Ag} \approx 2.4$ mol kg^{-1}.

The measurements on cell I were started with a two-phase system, $Ag(Br,NO_3)(s)$ - nitrate melt, and $\underline{C}_{Ag}$ was varied by additions

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of $AgNO_3$ in the range 0.8 mol $kg^{-1} \leq \underline{C}_{Ag} \leq$ 2.2 mol kg^{-1}. In all measurements $\underline{C}^{o}_{Ag}$ was kept as high as 2.2 mol kg^{-1} in order to minimize the effects of AgBr-precipitation in the diffusion layer between the half-cells. Stable emf readings were obtained within a few minutes in the study of unsaturated melts, whereas equilibrium times of 2-3 h were required when solid-liquid equilibria had to be established.

Analyses. The solubilities were determined by gravimetric analyses for bromide as AgBr. Silver was determined by electroanalytical precipitation of Ag on a rotating platinum cathode from hot aqueous cyanide solutions. The composition of the solid solution was calculated from the difference between added and found amounts of silver nitrate in the melt.

CALCULATIONS AND RESULTS

The following notations will be used:

A. Quantities referring to the emf measurements:

$\underline{E}_{obs}$ = the observed electromotive force of cells I and II.

$\underline{\varepsilon}$ = correction term, compensating for deviations from ideal Nernst behaviour.

$\underline{E}_{corr} = \underline{E}_{obs} + \underline{\varepsilon}$

$\underline{E}_o, \underline{k}$ = experimental parameters, defined by eqn. (1) below.

B. Quantities referring to the solubility measurements:

For the solid phase:

$\underline{x}_i$ = mole fraction of component $\underline{i}$ ($\underline{i}$ = 1 for AgBr and 2 for $AgNO_3$).

$\underline{a}_i$ = activity of component $\underline{i}$.

$\underline{f}_i = \underline{a}_i \underline{x}_i^{-1}$.

For the nitrate melt (all concentrations are expressed in molality units mol kg^{-1}, referring to equimolar $(K,Na)NO_3$ as solvent):

$\underline{C}_{Ag}$, $\underline{C}_{Br}$ = total concentration of silver(I) and bromide, respectively.

$[A]$ = concentration of species A.

$\underline{a}(NO_3)$ = the nitrate ion activity.

$\underline{\beta}_m = [Ag_{\underline{m}}Br^{(\underline{m}-1)+}][Ag^+]^{-\underline{m}}[Br^-]^{-1}$.

$\underline{K}_m = [Ag_{\underline{m}}Br^{(\underline{m}-1)+}][Ag_{(\underline{m}-1)}Br^{(\underline{m}-2)+}]^{-1}[Ag^+]^{-1}$.

$\bar{\underline{m}} = (\underline{C}_{Ag} - [Ag^+])\underline{C}_{Br}^{-1}$.

$\underline{M}$ = maximum value of $\underline{m}$.

Electromotive force measurements

In order to minimize the uncertainties in $\bar{\underline{m}}$ which are due to random errors in $\underline{E}_{obs}$ the measurements had to be restricted to melts with rather large total concentrations of silver and bromide. In the studied composition range, however, another complication arises, viz. that the ideal linear relationship between $\underline{E}_{obs}$ and $\lg[Ag^+]$ ceases to be valid when $\lg[Ag^+] \gtrsim 0$.[43] However, $\underline{E}_{obs}$ is still well reproducible. If we make the reasonable assumption that the presence of bromide in the melts does not affect the deviations from linearity as compared to halide-free systems, we may use the emf data collected in such melts in the calculation of a correction term $\underline{\varepsilon}$ to be added to $\underline{E}_{obs}$, yielding data $(\underline{E}_{corr}$; $\lg[Ag^+])$ which should be rationalized as

$$\underline{E}_{corr} = \underline{E}_o - \underline{k} \lg[Ag^+] \qquad (1)$$

The correction, which accounts mainly for liquid junction potentials and possible deviations from thermodynamic ideality, was tested in the bromide-free systems in series 3-5 (Table 1). The resulting parameter values ($\underline{E}_o$/mV ; $\underline{k}$/mV), which were used in the calculations pertaining to bromide containing melts in each series, were (37.6 ; 109.8), (37.4 ; 109.4) and (37.4 ; 109.8), respectively. These values of $\underline{E}_o$ and $\underline{k}$ are in excellent agreement with the theoretical Nernst equation parameters $\underline{RTF}^{-1} \ln \underline{C}^{o}_{Ag} = 37.4$ mV and $\underline{RTF}^{-1} \ln 10 = 109.7$ mV, and hence $[Ag^+]$ has been calculated from

$$\underline{E}_{corr} = (\underline{RT}/\underline{F}) \ln (\underline{C}^{o}_{Ag}/[Ag^+])$$

in series 1 and 2 (systems $Ag(Br,NO_3)(s)$ - nitrate melt). All experimental emf data are collected in Table 1.

In series 1 and 2 the ligand numbers were calculated by use of $\underline{C}_{Br}$ from the separate solubility data. In Fig. 1 the ligand numbers $\bar{\underline{m}}$ are plotted vs. $[Ag^+]$. The uncertainties in the $\bar{\underline{m}}$-values are of an order of magnitude of ± 0.2 as estimated from a reasonable assumption of random errors in $\underline{E}_{corr}$ of about ± 0.3 mV. As seen from Fig. 1 $\bar{\underline{m}}$ increases with $[Ag^+]$ from 3.3 to 3.7 in the concentration range investigated. Within the limits of experimental errors no systematic dependence of $\underline{C}_{Br}$ on $\bar{\underline{m}}$ at constant $[Ag^+]$ can be detected. This feature is taken as an indication of the absence of polynuclear complexes $Ag_{\underline{m}}Br_{\underline{n}}^{(\underline{m}-\underline{n})+}$ in observable amounts with a possible exception for species having $\underline{m}/\underline{n} \approx 3.5$.

No attempts at a further quantitative evaluation of the $\bar{\underline{m}}$-data in terms of definite stability constants have been made, but the important features of Fig. 1 which have been stressed here, give strong support to the interpreatation of the solubility data.

Solubility and distribution measurements

All data pertaining to the solubility and distribution measurements are collected in Table 2. As indicated by the magnitude of $\underline{x}_2$ there is a small but significant solubility of $AgNO_3$ in AgBr, and the following two heterogeneous equilibria have to be considered in the treatment of the data:

$$AgBr(ss) \rightleftarrows Ag^+ + Br^-$$

$$\underline{K}_1' = [Ag^+][Br^-]\underline{a}_1^{-1} \qquad (2)$$

$$AgNO_3(ss) \rightleftarrows Ag^+ + NO_3^-$$

$$\underline{K}_2' = [Ag^+]\underline{a}(NO_3)\underline{a}_2^{-1} \qquad (3)$$

Following the general principles outlined previously,[3] we set d ln $\underline{a}(NO_3) = 0$, since NO_3^- is effectively the only anion present in the nitrate melt, and arrive at

$$\ln \underline{a}_{1\underline{j}} = \int_{\ln [Ag^+]_o}^{\ln [Ag^+]_{\underline{j}}} - (\underline{x}_2/\underline{x}_1)\, d \ln [Ag^+] \qquad (4)$$

(The subscript $\underline{j}$ is used to indicate different quantities referring to the same actual system, and $[Ag^+]_o$ refers to a system with $\underline{x}_2 = 0$).

Since the experimental study was restricted to a range where $\underline{K}_1'$ and $\underline{\beta}_1$ can not be determined these constants have been taken from the thorough investigations of Cigén and Mannerstrand,[1,2] *viz.* $\underline{K}_1' = 3.00 \times 10^{-7}$ (mol kg^{-1})^2 and $\underline{\beta}_1 = 267$ (mol kg^{-1})$^{-1}$. The data have been treated according to

$$(\underline{C}_{Br}\underline{K}_1'^{-1}\underline{a}_1^{-1} - [Ag^+]^{-1} - \underline{\beta}_1)[Ag^+]^{-1} = \sum_{\underline{m}=2}^{\underline{M}} \underline{k}_{\underline{m}}[Ag^+]^{(\underline{m}-2)} \qquad (5)$$

From the least squares treatment of the left hand member as a function of $[Ag^+]$ it became evident that the summation in the right hand member had to be carried out to $\underline{M} = 4$, *viz.* complexes with ion charges +1, +2 and +3 should be considered. Since an existence of polynuclear (polybromic) species $Ag_{\underline{m}}Br_{\underline{n}}^{(\underline{m}-\underline{n})+}$ would require $\underline{m}/\underline{n} \approx 3.5$, to be in accordance with the potentiometric data, such species would have ion charges $\geq +5$. Therefore, it is concluded that only monobromic complexes are present in significant amounts. The solubilities are well reproduced assuming a stepwise formation of complexes Ag_2Br^+, Ag_3Br^{2+} and Ag_4Br^{3+} and the parameters $\underline{k}_{\underline{m}}$ of eqn. (5) are thus identified as $\underline{\beta}_{\underline{m}}$. Starting with $[Ag^+] \approx$ $\approx \underline{C}_{Ag} - 3\,\underline{C}_{Br}$ the calculations were iterated according to eqns. (4) and (5) to yield the final set of stability constants $\underline{\beta}_{\underline{m}}$ and free ligand concentrations $[Ag^+]$. The constants are given in Table 3.

The distribution of Ag(I) between the two phases has been treated as follows. Firstly, the activities $\underline{a}_2$ were estimated by integrating the relation

$$d \ln \underline{f}_2 = - (\underline{x}_1/\underline{x}_2)\, d \ln \underline{f}_1 \qquad (6)$$

Since $\underline{x}_1/\underline{x}_2$ appeared to be well approximated by

$$\underline{x}_1/\underline{x}_2 = [\sum_{\underline{\nu}=0}^{2} \underline{b}_{\underline{\nu}} (\ln \underline{f}_1)^{\underline{\nu}}]^{-1} \qquad (7)$$

the integration was performed analytically from the lower limit ($\ln \underline{f}_2 = 0$; $\ln \underline{f}_1 = 0$). For the most dilute solutions the errors in $\underline{x}_2$ and hence in $\ln \underline{f}_1$ prevent meaningful calculations. For that reason $\underline{a}_2$ and $\underline{f}_2$ have been omitted in Table 2 for these systems.

Secondly, setting $\underline{a}(NO_3) = 1$, the heterogeneous equilibrium constant $\underline{K}_2'$ is calculated as the average value of $[Ag^+]\underline{a}_2^{-1}$, yielding $\underline{K}_2' = (5.2 \pm 0.6) \times 10^2$ mol kg^{-1}. From $\underline{K}_1'$ and $\underline{K}_2'$ the equilibrium constant $\underline{K}_{12}'$ for the anion exchange reaction

$$AgBr(ss) + NO_3^- \rightleftarrows AgNO_3(ss) + Br^-$$

is obtained as $\underline{K}_{12}' = 5.8 \times 10^{-10}$ mol kg^{-1}.

DISCUSSION

In a recent paper[3] the influence of solvation of the uncomplexed central ion on the interpretation of data collected under conditions where the solvent activity decreases significantly was examined. In the present case we should have to consider an alkali cation solvation of the "uncomplexed" bromide ion. This possible effect has, however, been ignored in the calculations for the following two reasons. Firstly, there is no conclusive evidence found for specific halide-alkali metal ion interactions in mixed halide nitrate melts.[46-48] Secondly, even if it would be meaningful to speak of solvated bromide ions, preliminary calculations indicate that all complexes are present in fairly large relative amounts, and hence no serious errors in the stability constants due to the "solvation effects" should be expected.[3]

The over-all constants $\underline{\beta}_2$-$\underline{\beta}_4$, which are collected in Table 3, are all of the same order of magnitude. Hence, all complexes Ag_2Br^+, Ag_3Br^{2+} and Ag_4Br^{3+} are present simultaneously in comparable amounts in most of the melts investigated, which is the main reason why the uncertainties in $\underline{\beta}_2$ and $\underline{\beta}_3$ are rather large although the

spread in experimental solubility data is farily low. Table 3 also includes $\underline{\beta}$-values interpolated from the sets of constants determined by Sinistri and Pezzati[40] by solubility measurements at 275 °C and 300 °C. For $\underline{\beta}_2$ and $\underline{\beta}_3$ the agreement with their data is very good. It is also obvious that Sinistri and coworkers did not extend their measurements to the composition range where Ag_4Br^{3+} had to be considered.

Furthermore, we have estimated apparent constants $\underline{\beta}_1$ and $\underline{\beta}_2$ in hypothetical $KNO_3(l)$ and $NaNO_3(l)$ at 280 °C from the emf studies in the temperature range 400 °C - 500 °C.[34,35] The data published indicate a remarkably good constancy in $\Delta\underline{S}^{\ominus}$ and $\Delta\underline{H}^{\ominus}$ for the two first over-all complexation reactions over this temperature interval. These entities were estimated and used to compute $\underline{\beta}$-values at 553 K according to

$$\underline{\beta}_{\underline{m}} = \exp(\Delta\underline{S}^{\ominus}_{\underline{m}}/\underline{R} - \Delta\underline{H}^{\ominus}_{\underline{m}}/(\underline{R} \cdot 553))$$

Although this procedure leads to physically meaningless quantities, it may be of interest to note the agreement with those experimentally determined in $(K,Na)NO_3(l)$ (Table 3).

The potentiometric ligand concentration measurements in melts concentrated in solutes have clearly demonstrated the absence of systematic dependence of $\bar{\underline{m}}$ on $\underline{C}_{Br}$ in the composition range where a quantitative treatment of the complex equilibria is meaningful. Such a dependence should be expected if polybromic species with ion charges $\leq +3$ were present in significant amounts. The $\underline{\beta}$-values of Table 3 have been used to compute ligand numbers according to

$$\bar{\underline{m}} = (\sum_{\underline{m}=1}^{4} \underline{m}\underline{\beta}_{\underline{m}}[Ag^+]^{\underline{m}})(1 + \sum_{\underline{m}=1}^{4} \underline{\beta}_{\underline{m}}[Ag^+]^{\underline{m}})^{-1}$$

and the corresponding graph of $\bar{n}$ *vs.* $[Ag^+]$ is included in Fig. 1 to illustrate the perfect agreement between the emf and solubility measurements as interpreted in terms of mononuclear complexes only. It might, however, seem reasonable that polybromic complex cations should exist with the bromine atoms joined via a Br - Ag - Br linkage - an arrangment which has recently been found in solid Ag_2BrNO_3. This compound contains trigonal bipyramidal Ag_5Br--polyhedra, linked together by edges and corners.[45]

The relative distribution of bromide in different species is shown in Fig. 2 and the stepwise stability constants and quotients between them are collected in Table 4, where the relevant comparisons with aqueous solution data can also be made. In water no preference for Br to coordinate a certain number of ligands can be observed, whereas $\underline{n} = 2$ seems to be somewhat preferred at the expense of 3 in fused nitrate media, where Ag_3Br^{2+} amounts to at most about 30 % of $\underline{C}_{Br}$.

Finally it should be noted that although three terms in the right hand member of eqn. (5) were found to describe the solubilities sufficiently well in the composition range investigated, there is no obvious reason why the complex formation curve should stop definitely at $\bar{n} = 4$. The structures of the solid compounds $Ag_3I(NO_3)_2$ [21] and Ag_2BrNO_3 [45] suggest that a larger maximum coordination number might be possible. More detailed structure determinations of compounds of the above-mentioned type should give interesting information on the nature of the cationic complexes and the coordination of silver(I) to the halogen central atom.

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Table 1. Data from the electromotive force measurements.

C_{Br}/mol kg^{-1},	C_{Ag}/mol kg^{-1},	E_{obs}/mV,	E_{corr}/mV;

Series 1, cell type I:

0.0162,	0.912,	36.1,	44.8 ;	0.0246,	1.108,	29.0,	36.5 ;
0.0364,	1.325,	22.5,	28.7 ;	0.0470,	1.491,	18.8,	24.0 ;
0.0631,	1.717,	14.3,	18.4 ;	0.0804,	1.927,	10.8,	13.8 ;
0.0977,	2.119,	8.2,	10.5 ;				

Series 2, cell type I:

0.0128,	0.817,	40.5,	49.8 ;	0.0198,	1.003,	32.6,	40.7 ;
0.0300,	1.214,	25.8,	32.6 ;	0.0426,	1.432,	20.3,	25.9 ;
0.0548,	1.605,	16.6,	21.3 ;	0.0686,	1.788,	13.3,	17.1 ;
0.0815,	1.940,	10.8,	13.8 ;	0.1021,	2.161,	7.8,	10.0 ;

Series 3, cell type II:

0,	0.494,	60.2,	71.1 ;	0,	0.701,	44.8	54.7 ;
0,	0.903,	34.0,	42.4 ;	0,	1.143,	24.6	31.2 ;
0,	1.356,	18.0,	23.1 ;	0.0352,	1.391,	20.8	26.5 ;
0.0352,	1.567,	15.8,	20.3 ;	0.0352,	1.710,	12.3	15.7 ;
0.0352,	1.856,	9.1,	11.6 ;	0.0352,	2.029,	5.5	7.0 ;
0.0352,	2.188,	2.6,	3.1 ;				

Table 1 (continued):

Series 4, cell type II:

0,	0.766,	40.6,	50.0 ;	0,	0.988,	30.2,	37.9 ;
0,	1.204,	22.5,	28.6 ;	0,	1.422,	16.2,	20.8 ;
0,	1.656,	10.3,	13.3 ;	0.0589,	1.715,	13.9,	17.8 ;
0.0589,	1.844,	11.1,	14.2 ;	0.0589,	1.978,	8.0,	10.2 ;
0.0589,	2.122,	5.3,	6.7 ;	0.0589,	2.350,	1.2,	1.4 ;

Series 5, cell type II:

0,	0.893,	34.4,	42.8 ;	0,	1.161,	23.8,	30.2 ;
0,	1.411,	16.5,	21.1 ;	0,	1.652,	10.5,	13.5 ;
0,	1.877,	5.8,	7.3 ;	0.0764,	1.953,	10.0,	12.8 ;
0.0764,	2.101,	6.7,	8.7 ;	0.0764,	2.255,	4.0,	5.0 ;
0.0764,	2.400,	1.4,	1.6 ;				

Table 2. Solubility and distribution data.

C_{Ag} / mol kg^{-1}	C_{Br} / mol kg^{-1}	$x_2 \times 10^2$	a_1	f_1	$a_2 \times 10^2$	f_2	$\bar{m}$	$[Ag^+]$ / mol kg^{-1}	$[Ag^+][Br^-] \times 10^7$ / (mol kg^{-1})^2
0.2860	0.00201	0.03	1.000	1.000			2.57	0.2808	3.00
0.402	0.00297	0.05	1.000	1.000			2.81	0.394	3.00
0.495	0.00440	0.13	1.000	1.001			2.96	0.482	3.00
0.590	0.00662	0.27	0.999	1.002			3.08	0.570	3.00
0.695	0.00924	0.42	0.999	1.003			3.18	0.666	3.00
0.792	0.01195	0.43	0.998	1.002	0.15	0.34	3.27	0.753	2.99
0.900	0.01563	0.83	0.997	1.005	0.17	0.20	3.34	0.848	2.99
1.008	0.02018	0.85	0.996	1.004	0.19	0.22	3.40	0.939	2.99
1.110	0.02470	0.90	0.995	1.004	0.20	0.22	3.45	1.025	2.99
1.200	0.02922	1.40	0.995	1.009	0.20	0.14	3.48	1.098	2.98
1.297	0.03466	1.79	0.993	1.011	0.21	0.12	3.52	1.175	2.98
1.404	0.0419	1.93	0.992	1.012	0.23	0.12	3.55	1.255	2.98
1.501	0.0476	2.37	0.991	1.015	0.26	0.11	3.58	1.331	2.97
1.623	0.0560	2.31	0.989	1.012	0.28	0.12	3.60	1.421	2.97
1.713	0.0627	2.62	0.987	1.014	0.29	0.11	3.62	1.486	2.96
1.824	0.0716	2.70	0.986	1.013	0.30	0.11	3.64	1.563	2.96
1.931	0.0805	2.96	0.984	1.014	0.32	0.11	3.66	1.636	2.95
2.044	0.0914	3.10	0.983	1.014	0.34	0.11	3.67	1.708	2.95
2.186	0.1044	3.32	0.981	1.015	0.36	0.11	3.69	1.801	2.94

Table 3. Over-all stability constants for complexes $Ag_mBr^{(m-1)+}$ in alkali metal nitrate melts at 280 °C. The errors quoted are three standard deviations from the least squares calculations.

	$\beta_1 \times 10^{-2}$ / (mol kg^{-1})$^{-1}$	$\beta_2 \times 10^{-4}$ / (mol kg^{-1})$^{-2}$	$\beta_3 \times 10^{-4}$ / (mol kg^{-1})$^{-3}$	$\beta_4 \times 10^{-4}$ / (mol kg^{-1})$^{-4}$
This work, $(K,Na)NO_3$	2.67[a]	1.1 ± 0.4	2.2 ± 0.8	4.5 ± 0.5
Ref. 40, solubility data, $(K,Na)NO_3$[b]	3.5	0.8	2.4	-
Ref. 35, emf data, KNO_3[c]	2.6	2.9	-	-
Ref. 34, emf data, $NaNO_3$[c]	1.9	1.9	-	-

[a] From Ref. 2

[b] Interpolated values from experimental determinations at 275 °C and 300 °C.

[c] Apparent stability constants, extrapolated from investigations in the range 400 - 500 °C. Further details in the text.

Table 4. The stepwise stability constants and quotients in molten alkali nitrate and aqueous solution.

Medium	Quantity	$\underline{m} = 1$	$\underline{m} = 2$	$\underline{m} = 3$	$\underline{m} = 4$
H_2O, 20 °C, $\underline{I} = 0$	$K_{\underline{m}}/M^{-1}$	2.4×10^4[a]	475[b]	12[b]	-
$(K,Na)NO_3(l)$, 280 °C	$K_{\underline{m}}/(\text{mol kg}^{-1})^{-1}$	267[c]	40	2	2
H_2O, 20 °C, $\underline{I} = 0$	$K_{\underline{m}}/K_{(\underline{m}+1)}$	50	40	-	-
$(K,Na)NO_3(l)$, 280 °C	$K_{\underline{m}}/K_{(\underline{m}+1)}$	7	20	1	-

[a] Determined at 25 °C, Ref. 44

[b] Ref. 6

[c] Ref. 2

Figure texts.

Fig. 1. Ligand numbers $\bar{m}$ determined by emf measurements. Symbols: melts saturated in AgBr (●); C_{Br} = 76.4 mmol kg^{-1} (Δ); C_{Br} = = 58.9 mmol kg^{-1} (□); C_{Br} = 35.2 mmol kg^{-1} (○). The solid curve is calculated by use of the stability constants of Table 3.

Fig. 2. The distribution of bromide on different complex ions.

$$\alpha_m = [Ag_m Br^{(m-1)+}] C_{Br}^{-1}$$

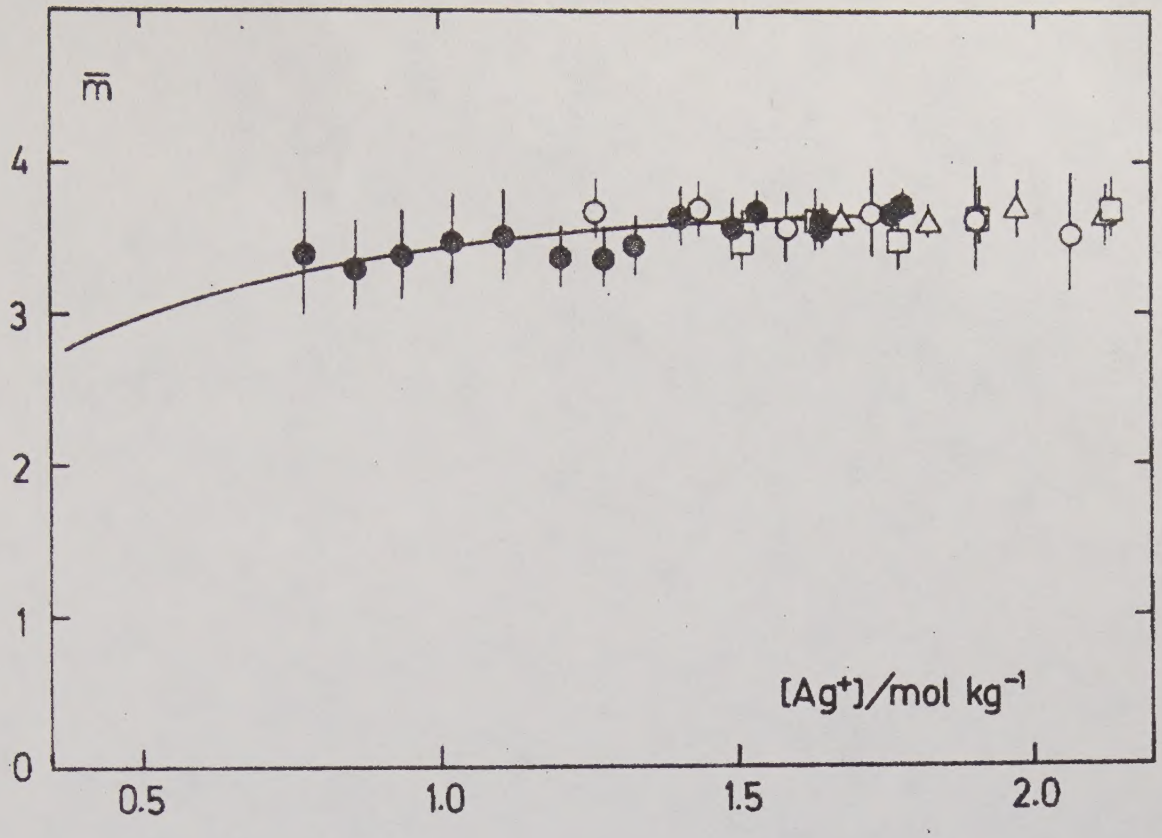
$\bar{m}$
4
3
2
1
0
0.5
1.0
1.5
2.0
[Ag+]/mol kg⁻¹

Fig. 1

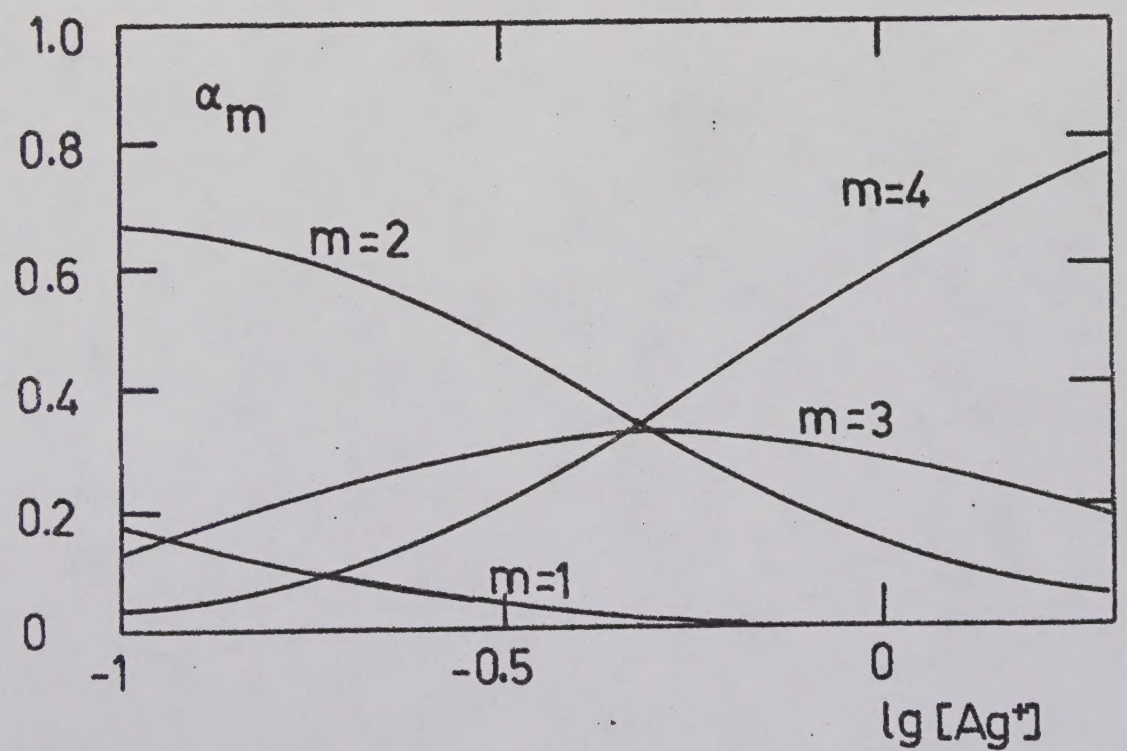
1.0
0.8
0.6
0.4
0.2
0
α_m
m=4
m=2
m=3
m=1
-1
-0.5
0
lg [Ag+]

Fig. 2

m
4
3
2
1
0
0.5
1.0
1.5
2.0
[Ag+]/mol kg⁻¹

Fig. 1

1.0
0.8
0.6
0.4
0.2
0
α_m
m=4
m=2
m=3
m=1
-1
-0.5
0
lg [Ag+]

Fig. 2